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FORMALDEHYDE ADDUCT OF LEVOPIMARIC ACID

A new intermediate from research at the Naval Stores Laboratory^{1/}

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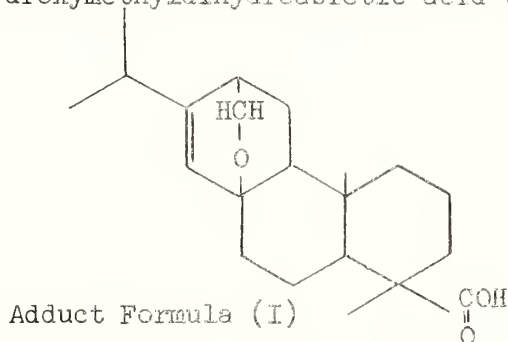
SOUTHERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION

DESCRIPTION: A new unusual reaction resulting from the Diels-Alder addition of formaldehyde across the homoannular diene system of levopimaric acid produces an adduct (I) which is unique in its reactions. Catalytic reduction of the adduct gives good yields of the glycol 6-hydroxymethyl-tetrahydroabietinol (II). A less drastic reduction of the acid isomerized adduct using palladium catalyst gives 6-hydroxymethyldihydroabietic acid (III).

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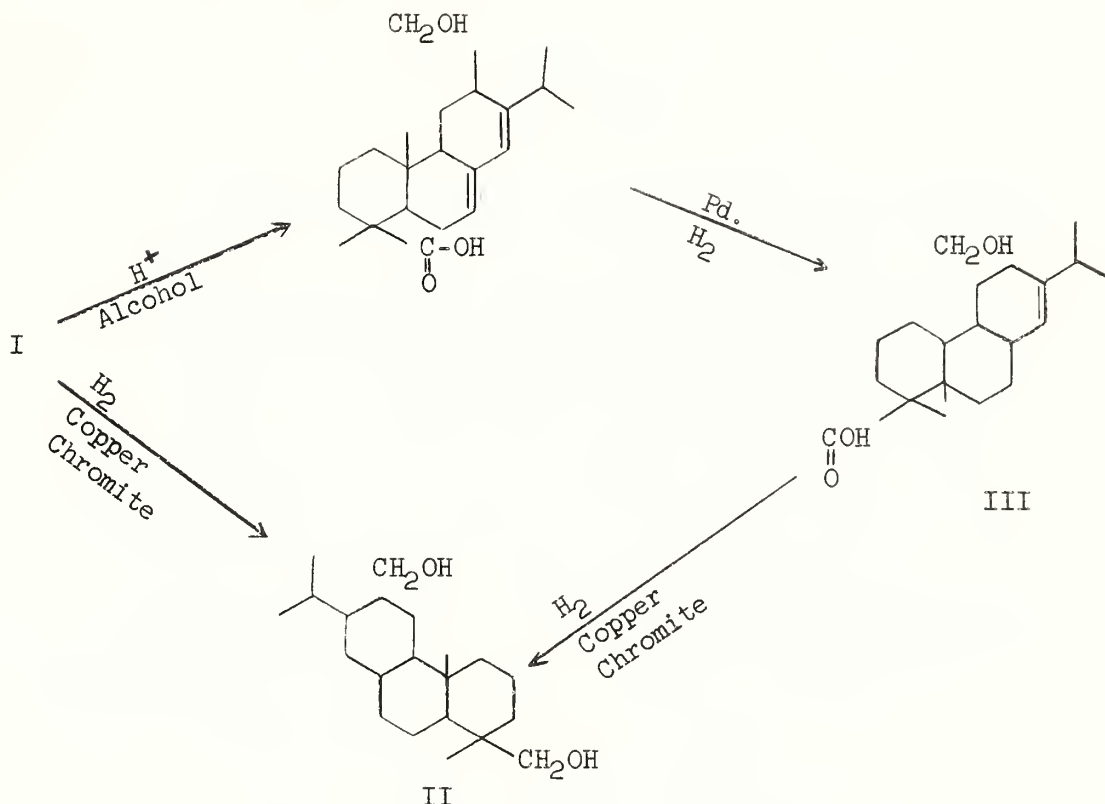
PROCESS:

For preparation of the adduct, levopimaric acid was slurried in mineral spirits and reacted with formaldehyde at 120-124°C. Resin acid products containing from 40 to 100 percent levopimaric acid can be made. The reaction was quenched by dilution with solvent-mineral spirits, heptane, ether, etc., and the adduct separated. For crystallization both ethanol and benzene were used to obtain pure adduct.

Recent laboratory developments indicate that it is also possible to obtain the crystalline adduct directly from pine gum by procedures readily adaptable to industry practices.

Current interest in the production of levopimaric acid may provide this product for simple conversion to the adduct.

^{1/} One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture, located at Olustee, Florida.

REACTION:

6-Hydroxymethyldihydroabietic acid. Prepared by dissolving the adduct in ethanol, adding 3 N HCl, neutralizing and hydrogenating over palladium catalyst. The product is recovered by diluting to 50 percent ethanol with water.

6-Hydroxymethyltetrahydroabietinol. Reduction of the adduct, the above hydroxyacid or polymer thereof with hydrogen, and copper chromite yields the desired glycol. Crude yield from dioxane is 50-70 percent. Improvement can be made by reworking and recycling the filtrate.

COSTS:

Assuming that levopimaric acid can be made in moderate quantities at a cost of under 40¢ per pound, it seems likely that the adduct can be made on a commercial scale for approximately 50¢ per pound.

POSSIBLE USES:

Plastics - especially polyesters, polyurethanes, and epoxy resins, and others.

Agricultural - pesticides, fungicides; reaction products with acrylonitrile.

Drugs - intermediate in the preparation of steroids, bactericidal formulations, suntan formulations and hydrazide as blood pressure depressant.

- REFERENCES: Isolation of Resin Acid Mixtures Rich in Levopimaric Acid from Pine Gum. Summers, H.B., Jr.; Lloyd, W. D.; and Hedrick, G. W. I&EC Prod. Res. & Develop., 2(3): 173-177 (1963)(Reprint No. 2595)
- Chemistry of Resin Acids. I. The Reaction of Levopimaric Acid with Formaldehyde. Parkin, B.A., Jr.; and Hedrick, G. W. J. Org. Chem. 30, 2356 (1965) (Reprint No. 2967)
- Composition of Resin Acid Mixtures Rich in Levopimaric Acid and Preliminary Cost Estimates. Summers, H. B., Jr.; Parkin, B. A., Jr.; Joye, N. M., Jr.; and Hedrick, G. W. I&EC Prod. Res. Develop. 4, 221-223 (1965) (Reprint No. 3051)

Additional information, reprints, and limited samples may be obtained from:

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